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Description

The present invention relates to a process for the production of paper with wet strength properties using polyamine or polyamideamine based wet strength resins. More particularly the invention relates to a process wherein the wet strength resin is added to the stock at a low pH and wherein the pH of the wet web is increased before the drying.

Polyamine resins and polyamideamine resins, which also are called polyamide polyamine resins or polyamine polyamide resins, are well known additives in papermaking for the production of wet strength paper. These cationic thermosetting resins are modified with cross-linking agents such as epihalohydrins, primarily epichlorohydrin, diisocyanates and dichloro isopropanol. The main use of these resins is for the production of soft crêpe paper, since they do not impair softness or absorption capability. The with cross-linking agents modified polyamine and polyamideamine resins are normally used as additives to the stock at neutral or alkaline pH, usually within the range of from 6 to 11 and most often at a pH of from 6 to 8, since it is considered that this gives the best effect.

According to the present invention it has been found that the effect when using polyamine and polyamideamine resins, modified with cross-linking agents such as e.g. epichlorohydrin, can be considerably improved if the resins are added to the stock at an acid pH whereafter the pH, in a later stage of the paper production, before the drying, is increased for curing of the resin. By addition of the resin to the stock at a low pH the retention of the resin to the fibres is substantially improved. Through the process of the invention a higher wet strength can be obtained than that previously obtained when the resins were used at a neutral or alkaline stock-pH. The process of the invention also makes it possible to decrease the amount of modified resin required to obtain a certain degree of wet strength. Both this possibility and the increased retention are of considerable importance with regard to the environmental impact by resins with halogenated cross-linking agents, such as epichlorohydrin, since the outlet in the waste water of halogenated organic compounds can be decreased.

The present invention thus relates to a method for the production of paper, board and paperboard, ie cellulose based products in web or sheet form, as defined in the patent claims.

As has been mentioned, the polyamine and polyamideamine resins modified with cross-linking agents are per se well known wet strength resins at paper production. Any such resin can be used. The present invention relates particularly to the production of paper using modified polyamideamine resin. The polyamideamine resins modified with cross-linking agents which can be used in the present process are cationic, water soluble and thermosetting. These types of resins are based on reaction products of cross-linking agents and polyamineamide originating from aliphatic dicarboxylic acids or derivatives of these, such as esters, and polyalkylene polyamines such as diethylenetriamine, tetraethylenepentamine, methylbisaminopropylamine etc.. As cross-linking agents for these resins diisocyanates, dichloro isopropanol and epihalohydrins can for example be used. Preferred polyamideamine resins are such which are modified with epihalohydrins and particularly with epichlorohydrin.

According to the present process the polyamideamine resin is added to the stock at a pH of not higher than 6.5 and suitably at a pH of not higher than 5. The lower limit for the pH is suitably 4 and it is especially preferred that the pH is within the range of from 4 to 5. At the production of paper the pH in the stock supplied to the paper machine can vary within the range of from 3 to 11. Required adjustment of the pH in the stock to the paper machine can suitably be made in the machine box. The pH adjustment for a more acid pH can be carried out with alum but, in order to increase the possibility to reach a z-potential of 0 in the stock as far as possible, it is preferred to make the pH adjustment with sulfuric acid. If the pH of the supplied stock has to be increased alkali, such as sodium-hydroxide, is suitably used. The modified polyamine or polyamideamine resin can be added to the stock in the machine box or at a suitable point between this and the wire and it is suitably added to the stock in the form of a diluted aqueous solution of 1 to 2%, as conventionally. The wet strength resins are usually used in amounts of from about 0.2 to about 3 per cent by weight, calculated as dry on the dry content of the stock, fibers and optional fillers. With the present process, which gives increased retention, the amounts can be considerably reduced, if so desired. Thus, according to the present process, good effect can be obtained with from 0.1 per cent by weight of the polyamine or polyamideamine resin, calculated as dry on the dry substance of the stock. The upper limit is not critical for the wet strength effect and amounts up to about 3 per cent by weight can be used. For reasons of economy, and in order to make use of the advantages with regard to environment which are offered, it is suitable to use amounts up to 2.0 per cent by weight. It is particularly suitable to use amounts within the range of from 0.2 to 1.0 per cent.

Through the addition of the modified wet strength resin at a low stock pH an improved retention of the resin is obtained. The pH is then to be adjusted to an alkaline pH for curing of the resin. This adjustment of pH is made in the wet web formed on the wire, before the drying. The stock supplied to and dewatered on the wire usually has a dry substance content of from 0.1 to 0.5 per cent by weight. The wet web at the end of the

wire has a dry content of from about 15 to about 20 per cent by weight. After the press section of the paper machine the wet web has a dry content of about 25 to about 35 per cent by weight. The pH adjustment according to the present invention is made to the wet web before the drying, ie when the web has a dry content of from about 15 to about 35 per cent by weight. The pH adjustment of the wet web is suitably made in connection with rolls or other equipment at the final end of the wire, for example at dandy rolls or via press felts. For machines which are equipped with yankee cylinders there is normally a spray equipment in direct connection to this cylinder by means of which chemicals such as picking chemicals and softeners are added. At such machines it is suitable to carry out pH adjustment by spraying at this dosage point. According to the present invention the pH is to be adjusted so that the aqueous phase of the wet web gets a value of not lower than 7. The pH adjustment is suitably carried out to a pH not lower than 8. The upper limit for the pH is suitably at 10 and it is particularly preferred that the pH is within the range of from 8 to 10. The pH adjustment in the wet web is carried out using a suitable alkalizing solution. The pH can be adjusted with for example hydroxide or bicarbonate and then particularly sodium- and ammonium hydroxide and sodium- and ammonium bicarbonate respectively. Further, it is, of course, suitable to work with alkaline solutions of fairly high concentration in order to avoid adding too much water which then has to be dried off. However, so strong solutions that discolouring of the cellulose occurs are of course to be avoided.

As has been stated above, the present process gives advantages with regard to retention and level of wet strength. It has also been found that a certain increase of the rate of curing is obtained which means that storage times can be shortened. The present process can be used for the production of wet strength paper of different types where modified polyamine or polyamideamine resins are used, and particularly for the production of soft crêpe paper such as tissue for household and sanitary purposes since softness and absorption properties are maintained. At the paper production according to the invention other paper chemicals such as hydrophobing agents and retention agents can be used.

The invention is further illustrated in the following examples which, however, are not intended to limit the same. Parts and per cent relate to parts by weight and per cent by weight, respectively, unless otherwise stated.

Example 1

Paper having a grammage of 70 g/m² was produced on an experimental papermaking machine from bleached sulphate pulp beaten to 24°SR. As the sole additive a wet strength resin of polyamideamine type modified with epichlorohydrin was used. The resin was added in an amount of 0.4 per cent by weight based on dry pulp. In comparative test 1a) the wet strength resin was added to a stock having a pH of 6 to 7 and no subsequent pH adjustment was made. In test 1b), according to the invention, the wet strength resin was added to a stock having a pH of 4 to 5. The pH in the web formed on the wire was then raised to between 7 and 7.4 before pressing and drying by making the cleaning water to the dandy roll alkaline.

The wet strength, in km breaking length, of the paper produced in the tests was measured according to SCAN P 38-80. The wet strength was measured both after storage for two days and nights at room temperature and after this storage and further curing at 105°C for 1 hour and 2 hours respectively.

Test	Wet strength km breaking length		
	2 days and nights	+1 h 105°C	+ 2 h 105°C
1a)	1.64	2.00	2.20
1b)	1.82	2.15	2.50

As evident the process of the invention gave an improvement both of the wet strength after storage for two days and nights and of full wet strength after additional curing. The latter shows that in addition to a more rapid development of the wet strength an improved retention of the wet strength resin has also been obtained.

Example 2

The following tests were carried out on a larger experimental papermaking machine, with a capacity of 0.5 tons per hour, for the production of tissue. The machine had an open white water system and a spray box before the drying cylinder. The pulp was bleached sulphate beaten to 23° SR. Tissue having a grammage of 22 g/m² and a crêping degree of 22% was produced. The wet strength resin which was used was an epichlorhydrin modified polyamideamine resin which was added in an amount of 1.1 per cent by weight, based on

dry pulp. As z-potential regulator towards zero, anionic carboxymethyl cellulose was used. In the tests wherein the pH of the wet web was adjusted this was carried out by spraying with bicarbonate solution. Th wet strength of the produced tissue paper, in %, was measured according to SCAN P 58-86. The retention of added wet strength resin was also measured.

Test no	pH in stock	pH adjust.	pH in paper*	Wet Strength %	Retention %
1	6.5	no	5.4	29	45
2	4.5	yes	6.3	36	58
3	6.5	no	5.5	40	80
4	4.6	yes	7.9	45	89

*pH in the paper was measured as extract pH in finished paper. As evident from test 1 in which no pH adjustment was made a stock pH of 6.5 for the stock in question corresponded to a pH in the paper of 5.4. This pH was thus about 1 unit lower than the stock pH, depending on the pH of the fibre material. Thus the pH adjustment in tests 2 and 4 of the wet web have given this pH values of about 7.3 and 8.9, respectively.

In tests 3 and 4 the z-potential was adjusted towards 0, but no such adjustment was made in the tests 1 and 2.

As evident a substantial improvement of both the retention of wet strength resin and the wet strength of the finished paper was obtained by using the process of the invention.

Claims

1. A process for the production of wet strength paper, board and paperboard which comprises addition of polyamine- or polyamideamine wet strength resin modified with cross-linking agent to an acid stock of cellulose containing fibres, forming and dewatering of the stock on a wire and subsequent drying, characterized in that the wet strength resin is added to the stock at a pH not higher than 6.5 and in that the pH of the aqueous phase of the wet web leaving the wire is adjusted to a value of not lower than 7 before the drying.

2. A process according to claim 1, characterized in that the addition of the resin is made at a stock pH of not higher than 5.

3. A process according to claim 1 or 2, characterized in that the pH of the stock has been adjusted by addition of sulphuric acid.

4. A process according to claim 1, characterized in that the pH in the aqueous phase of the wet web is adjusted to a value of not lower than 8.

5. A process according to claim 1 or 4, characterized in that the pH in the aqueous phase of the wet web is adjusted by addition of a compound containing hydroxide or bicarbonate groups.

6. A process according to any of the preceding claims, charact rized in that th wet strength resin is a polyamideamine resin.

7. A process according to claim 6, characterized in that the polyamideamine resin is modified with epichlorohydrin.

Patentan prüche

1. Verfahren zur Herstellung von naßfestem Papier, Karton und Pappe, umfassend die Zugabe eines Polyamin- oder Polyamidamin-Naßfestigkeits-Harzes, das durch ein Vernetzungsmittel modifiziert ist, zu einem sauren Papierrohstoff aus cellulosehaltigen Fasern, Formen und Entwässern des Papierrohstoffes auf einem Drahtnetz und nachfolgend Trocknen, dadurch gekennzeichnet, daß das Naßfestigkeits-Harz zu dem Papierrohstoff bei einem pH von nicht höher als 6,5 zugegeben wird, und daß der pH der wäßrigen Phase der feuchten Papierbahn, die das Drahtnetz verläßt, auf einen Wert nicht unter 7 vor dem Trocknen eingestellt wird.

2. Verfahren nach Anspruch 1, dadurch gekennzeichnet, daß die Zugabe des Harzes bei einem pH des Papierrohstoffes von nicht höher als 5 durchgeführt wird.

3. Verfahren nach Anspruch 1 oder 2, dadurch gekennzeichnet, daß der pH des Papierrohstoffes durch Zugabe von Schwefelsäure eingestellt wird.

4. Verfahren nach Anspruch 1, dadurch gekennzeichnet, daß der pH in der wäßrigen Phase der feuchten Papierbahn auf einen Wert nicht unter 8 eingestellt wird.

5. Verfahren nach Anspruch 1 oder 4, dadurch gekennzeichnet, daß der pH in der wäßrigen Phase der feuchten Papierbahn durch Zugabe einer Verbindung, die Hydroxid oder Bicarbonatgruppen enthält, eingestellt wird.

6. Verfahren nach einem der vorhergehenden Ansprüche, dadurch gekennzeichnet, daß das Naßfestigkeits-Harz ein Polyamidaminharz ist.

7. Verfahren nach Anspruch 6, dadurch gekennzeichnet, daß das Polyamidaminharz mit Epichlorhydrin modifiziert ist.

Revendications

1. Procédé de fabrication d'un papier, carton et papier cartonné résistants à l'état humide qui comprend l'addition d'une résine résistante à l'état humide de polyamine ou de polyamideamine modifiée par un agent de réticulation à un matériau acide de fibres contenant de la cellulose, la mise en forme et la déshydratation du matériau sur une toile métallique et le séchage ultérieur, caractérisé en ce que la résine résistante à l'état humide est ajoutée au matériau à un pH qui n'est pas supérieur à 6,5 et en ce que le pH de la phase aqueuse de la nappe humide quittant la toile métallique est ajusté à une valeur qui n'est pas inférieure à 7 avant le séchage.

2. Procédé selon la revendication 1, caractérisé en ce que l'addition de la résine est faite au niveau d'un pH du matériau qui n'est pas supérieur à 5.

3. Procédé selon la revendication 1 ou 2, caractérisé en ce que le pH du matériau a été ajusté par addition d'acide sulfurique.

4. Procédé selon la revendication 1, caractérisé en ce que le pH dans la phase aqueuse de la nappe humide est ajusté à une valeur qui n'est pas inférieure à 8.

5. Procédé selon la revendication 1 ou 4, caractérisé en ce que le pH dans la phase aqueuse de la nappe humide est ajusté par addition d'un composé contenant des groupes hydroxyde ou bicarbonate.

6. Procédé selon l'une quelconque des revendications précédentes, caractérisé en ce que la résine résistante à l'état humide est une résine de polyamideamine.

7. Procédé selon la revendication 6, caractérisé en ce que la résine de polyamideamine est modifiée avec de l'épichlorohydrine.